III.A.6 Development of Metal-Supported SOFC

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Objectives

- Reduce the cost and increase the reliability of solid oxide fuel cell (SOFC) components through the introduction of inexpensive metal supports.
- Improve SOFC electrode performance through metal salt infiltration.
- Develop anti-corrosion coatings for stainless steel components to inhibit scale growth and Cr volatilization and to maintain high electronic conductivity.

Approach

- Develop low-cost coating technology for stainless steel components.
- Infiltrate cobalt nitrate into reproducible lanthanum strontium manganite (LSM) and LSM/YSZ air electrode structures.
- Conduct long-term testing of metal-infiltrated cells to determine aging effects.
- Determine and optimize sintering profiles for LSM-YSZ cathodes to match with sintering of yttria-stabilized zirconia (YSZ) thin-film electrolyte.
- Determine baseline power curves for alternative anodes on cathode-supported cells.

Accomplishments

- Doubled the performance of anode- and cathode-supported SOFCs at reduced operating temperature (650°C).
- Developed anti-corrosion coating based on reaction of Mn-Co spinel with stainless steel; this coating reduced corrosion rate by a factor of 10 and survived 120 rapid thermal cycles with no evidence of spallation.
- Developed a unique method to infiltrate anode and cathode catalysts into porous structures in a **single processing step**, producing sufficient catalyst loading for high-performance electrodes. A wide range of perovskite compositions can be produced from this proprietary technology. A fine-grained structure that is highly catalytic is produced, leading to excellent performance.
- Long-term testing (100 hours) of metal-nitrate-infiltrated cells has indicated stable performance for this period of time. Longer-term (1000 hours) tests will be performed in the next quarter.
- Successfully determined and modified sintering profiles for LSM-YSZ substrates to match YSZ thin-film electrolyte, and consequently produced high-quality cathode-supported cells.
- Used cathode-supported cells to evaluate alternative anodes (sulfur tolerant). Initial testing at Lawrence Berkeley National Laboratory (LBNL) indicates that further development of alternative anodes is needed.

Future Directions

- Determine the window of stability for electrode enhancement by nano-infiltration: examine the effects of temperature, degree of infiltration, and chemical composition on long-term stability of performance boost, and recommend an operational range for the improved electrodes.
- Set up equipment for the accurate determination of volatile Cr species produced when moist air reacts with stainless steel. This is a critical parameter for the commercialization of low-cost fuel cell stacks having stainless steel components.
- Determine the effect of anti-corrosion coatings on Cr volatilization from stainless steel.
- Determine the window of stability for the use of steel components in high-temperature solid oxide fuel cells from 600 to 900°C for both stationary power applications (50,000 - 100,000 hours) and transportation applications (5,000 - 10,000 hours).

Introduction

The main goal of the LBNL project is to support industrial Solid State Energy Conversion Alliance (SECA) teams in their effort to commercialize solid oxide fuel cell technology that meets the SECA performance and cost targets. In order to achieve the aggressive SECA goals, it is necessary to reduce the cost of solid oxide fuel cell components through the introduction of inexpensive materials while maintaining the high levels of performance possible with thin-film electrolytes. Developers are also compelled to lower the operating temperature of SOFC systems while maintaining high system efficiency. Accordingly, in FY 2004 the LBNL core effort is focused on the use of catalyst infiltration to improve electrode performance at low temperature, the development of cathode-supported architectures for sulfur-tolerant anodes, and electrochemical characterization of the improved electrodes during transient and extended operation

Approach

Among the complexities of SOFC development is the high degree of interactivity between SOFC materials at the processing temperature and/or during cell operation. This interaction can negate improvements made to isolated components and lead to fuel cell or stack failure. Accordingly, the LBNL team uses a highly integrated approach for the development of low-cost SOFC components, testing improvements on realistic cell structures with close attention to the manufacturability of technical innovations. The LBNL team also talks routinely with component manufacturers to assess the commercial viability of its SOFC improvements. The LBNL group uses standard electro-analytical techniques for the characterization of fuel cell components such as AC impedance spectroscopy, potentiostatic and galvanostatic evaluation, as well as current-interrupt and related electrochemical techniques. Our group has also fabricated a sensitive transpiration apparatus to determine the Cr volatilization rates for coated and uncoated stainless steel samples. In this way, we can determine the effectiveness of coatings developed at LBNL in terms of the electronic conductivity of the coating, compatibility with anode and cathode composition, oxidation resistance, and minimization of Cr evaporation in the fuel cell environment. It is anticipated that technical innovations developed at LBNL and careful characterization of structures fabricated with such improvements will lead to successful technology transfer to the industrial teams.

Results

In order to ensure long life for SOFC stacks, a number of developers are considering reducing the fuel cell operating temperature from 800-900°C to 600-800°C. Since ionic transport and electrode kinetics are thermally activated, the power density of fuel cell stacks decreases with temperature. Accordingly, the LBNL team has been developing nano-catalysts that can be infiltrated into the fuel cell electrodes to boost the low-temperature performance and thereby offset the negative effect of lower operating temperature on power density. As can be seen in Figure 1, the peak power density of an anode-supported thin-film SOFC cell was ***increased by a***

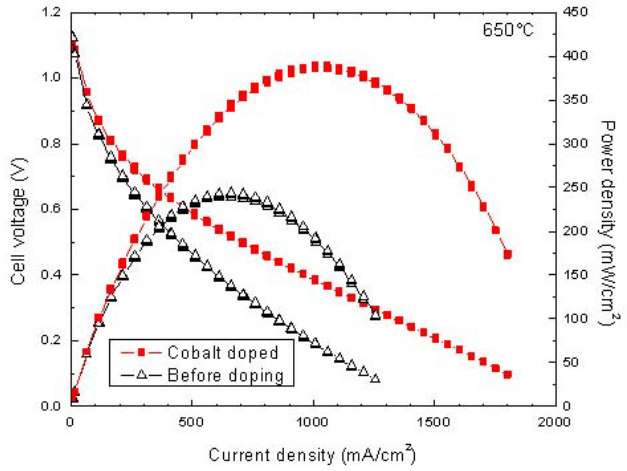

Figure 1. 650°C Performance of Anode-Supported Thin-Film Cell with LSM-YSZ Cathodes

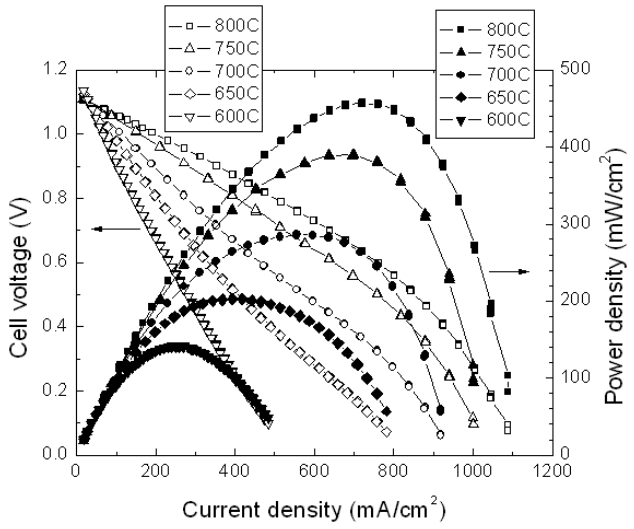

Figure 2. 600-800°C Performance of Cathode-Supported SOFC with Catalyst Infiltration

factor of 2 at 650°C. We have seen similar performance improvements for both anode- and cathode-supported thin-film SOFCs (Figures 1 & 2). A key issue for this approach is that the improvement in power density at reduced temperatures is stable over the operating lifetime of the SOFC stack. The LBNL group is currently investigating the time-dependence of the performance of electrodes having nano-catalyst infiltration. LBNL has also done transmission electron microscope (TEM) investigations of electrode structure as a function of catalyst infiltration; as can be seen from Figure 3, the

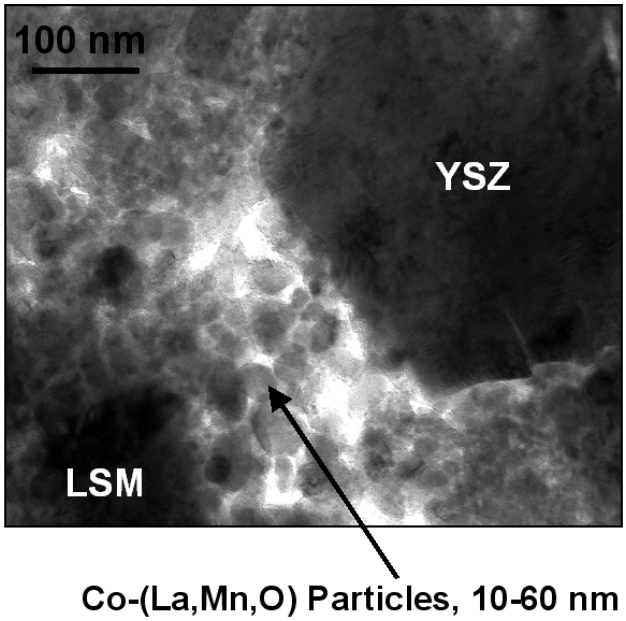

Figure 3. TEM Image of Infiltrated Nano-Catalysts after 100 Hours at 800°C

presence of 10-60 nm catalyst centers is observed in the modified structure. Such modified electrodes have been tested for periods of 100 hours continuous operation with no indication of performance deterioration. However, longer tests of 1000 hours or more are needed to project the long-term stability of the modified low-temperature electrodes.

The LBNL team has also developed process technology for the fabrication of cathode-supported SOFCs. This work was initiated to support the development of alternative anodes for sulfur-tolerant SOFCs. To date, the majority of work in sulfur-tolerant anodes has been focused on $SrTiO_3$-based electrodes. However, the titanate electrodes tend to react with the YSZ electrolyte when co-fired in an anode-supported geometry. Consequently, the LBNL group launched the development of cathode-supported cells so that alternative anodes can be bonded to the cathode-supported structure at reduced temperatures. As can be seen from Figure 2, the performance of the cathode-supported SOFC is quite reasonable at temperatures as low as 650°C. Initial testing of alternative anodes on the cathode-supported cells indicates that further improvements are needed.

Another critical issue for the development of SOFC stacks utilizing metal components is the

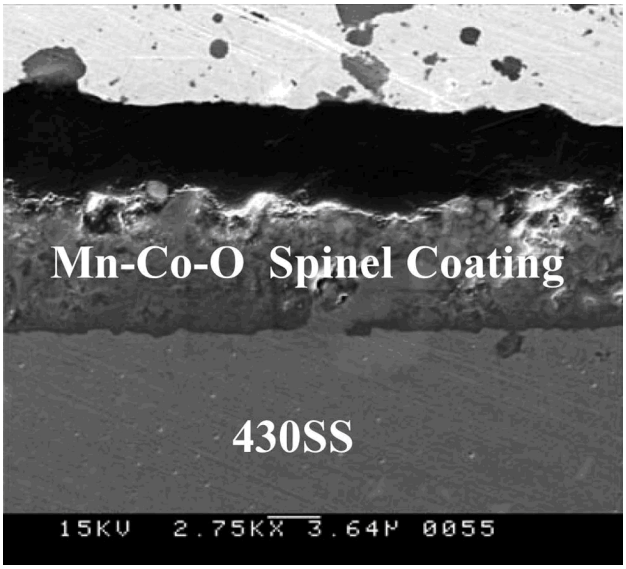

Figure 4. Protective Coating on Stainless Steel after 120 Rapid Thermal Cycles between Room Temperature and 800°C

development of low-cost coatings to reduce the oxidation of the metal as well as block the vaporization of volatile $Cr(OH)_2O_2$ produced from the reaction of moist air with the Cr_2O_3 scale. The LBNL group developed a technique whereby a colloidal $MnCo_2O_4$ powder is spray-coated onto 430 stainless steel and bonded at 850°C. At 850°C, this coating exibits a ***factor of 10 improvement in oxidation rate and resistivity*** compared with the uncoated 430 stainless steel. Another critical aspect of any coating is its ability to withstand thermal cycling. Coated and un-coated 430 stainless steel samples were subjected to 120 rapid thermal cycles; the uncoated samples showed significant spallation of the chromia scale, while the coated samples showed no evidence of thermal cycling damage (see Figure 4).

Future work will include refinement of the metal infiltration process and long-term testing of the stability of the performance improvement. We have completed the assembly of the transpiration measurement apparatus and will initiate studies on the volatilization of Cr from coated and un-coated stainless steel samples. As we continue to improve electrode performance at reduced temperatures and the behavior of steel components in aggressive environments, we will then initiate testing of small SOFC stacks incorporating such improvements to assess the viability of the technology for transfer to the industrial teams.

Conclusions

- Infiltration of catalytic metal nitrates into porous fuel cell electrodes improves the peak power performance by as much as a factor of 2 at reduced temperatures.
- Anti-corrosion coating based on reaction of Mn-Co spinel with stainless steel reduces the corrosion rate by a factor of 10, exhibits much higher electronic conductivity than the native scale, and survives hundreds of rapid thermal cycles with no evidence of spallation.
- Long-term testing (100 hours) of metal nitrate-infiltrated cells indicates stable performance. Longer-term (1000 hours) tests will be performed in the next quarter.
- The performance of cathode-supported thin-film cells is quite reasonable, but somewhat lower than anode-supported structures
- Initial testing at LBNL indicates that further development of alternative anodes is needed.

FY 2004 Publications/Presentations

1. *Protective Coating on Stainless Steel Interconnect for SOFCs: Oxidation Kinetics and Electrical Properties*, Xuan Chen, Peggy Y. Hou, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe, submitted to Solid State Ionics.

2. *Catalyst-Infiltrated Supporting Cathode for Thin-film SOFCs*, Keiji Yamahara, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe, submitted to Solid State Ionics.

3. *Ionic Conductivity of Stabilized Zirconia Networks in Composite SOFC Electrodes*, Keiji Yamahara, Tal Z. Sholklapper, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe, submitted to Solid State Ionics.

4. *Development of Low-Cost Metal Supported SOFCs,* Steven J. Visco, Craig P. Jacobson, Lutgard C. De Jonghe, 2003 Fuel Cell Seminar, November 3-7, 2003, Miami Beach, Florida.

5. *Co-Fired Cathode Supported Thin Film IT-SOFC,* Ionel C. Stefan, Keiji Yamahara, Mariza Marrero-Cruz, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe, Electrochemical Society 2003 Meeting, Orlando, Florida.

6. *The Effect of Lithium Doping on Ceria-Based Electrolyte Materials,* Craig P. Jacobson, Mariza Marrero-Cruz, Eric P. Hong, Steven J. Visco, and Lutgard C. De Jonghe, 8th International Symposium on Ceramics in Energy Storage and Power Conversion Systems, January 28, 2004.

7. *Modification of Electrode Architectures for Reduced Temperature SOFCs*, Craig P. Jacobson, Keiji Yamahara, Liming Yang, Steven J. Visco, and Lutgard C. De Jonghe, 8th International Symposium on Ceramics in Energy Storage and Power Conversion Systems, January 28, 2004.

8. *Improving the Electrochemical Performance of Metal Supported SOFCs*, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe, 8th International Symposium on Ceramics in Energy Storage and Power Conversion Systems, January 28, 2004.

9. *Co-Fired LSM Supported Thin-Film SOFCs with Infiltrated Catalysts*, Lutgard C. De Jonghe, Keiji Yamahara, Craig P. Jacobson, and Steven J. Visco, 6th European Solid Oxide Fuel Cell Forum.

10. *Alloy Supported Thin-Film SOFCs*, Lutgard C. De Jonghe, Craig P. Jacobson, Steven J. Visco, 6th European Solid Oxide Fuel Cell Forum.

11. *Interfaces in Solid Oxide Fuel Cells*, Lutgard C. De Jonghe, Keiji Yamahara, Craig P. Jacobson, and Steven J. Visco, Lake Louise 2003.

Special Recognitions & Awards/Patents Issued

1. United States Patent 6,682,842, January 27, 2004, Composite electrode/electrolyte structure, Steven J. Visco, Craig P. Jacobson and Lutgard C. De Jonghe.

2. United States Patent 6,740,441, May 25, 2004, Metal current collect protected by oxide film, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe.

3. United States Patent Application, Planar electrochemical device assembly, June 17, 2004, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe.

4. United States Patent Application, Electrochemical cell stack assembly, February 5, 2004, Craig P. Jacobson, Steven J. Visco, and Lutgard C. De Jonghe.